

# MESOSCALE MODELING OF ELECTROCHEMICAL CRYSTAL GROWTH IN ADVANCED LITHIUM BATTERIES

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## SUMMARY

A multiphysics phase-field model is being developed to simulate electrochemically driven microstructural evolution in advanced lithium batteries, considering multicomponent diffusion, stress equilibration, electrostatics and phase-stability analysis.

## INTRODUCTION

Efficient electrical energy storage is an important aspect of a secure and sustainable energy future and advanced Lithium batteries are a key technology to suit this need. The understanding of fundamental processes and material properties involved in these batteries is being developed in a multiscale approach, a key aspect of which is the mesoscale (1  $\mu\text{m}$  – 1 nm). The mesoscale focuses on the dynamically evolving microstructure of the Lithium oxide growth and dissolution during charging and discharging cycles. The oxide microstructure influences the charge / discharge rates through the surface area available for reaction and the diffusion pathways of charge carriers. Also of consideration are the stresses in the interface due to volume changes during phase changes, which can lead to mechanical failure. Finally, local heat generation and transport can affect the safety and range of applications of this technology.

The phase-field model is a mesoscale modeling approach well suited to this application as it integrates dynamically evolving interfaces driven by thermodynamic forces and continuum scale transport phenomena, with mechanisms and properties revealed by atomic and electronic structure level calculations. It is commonly applied to solidification problems using fundamental principals of entropy generation and is readily transferable to electrochemical crystal growth.

## CURRENT WORK

In the current work, two continuum scale models of general nanoscopic systems are described to explore electrochemical crystal growth considering evolving microstructure, electrostatics and diffusion of charged species.

In the first model, the interface is represented as a sharp boundary between phases consistent with the Stefan formulation. The system is solved in a moving frame of reference, the velocity of which is determined by the diffusion of the ionic species adjacent to the interface. This model is conceptually accurate for a specific case of interface movement and so useful for checking the more

advanced phase-field model.

The second model employs a diffuse interface phase-field model on a fixed mesh in multiple dimensions. This approach allows for complex interface morphologies and naturally includes phenomena such as excess interfacial energies associated with curved interfaces. The drawback of using the phase-field model compared to the Stefan formulation is significantly higher computational expense, which depends on, among other factors, the user-selected width of the interface. A point of connection is offered between the phase-field and Stefan models as the former must converge to the latter in the sharp interface limit, i.e.: as the interface width approaches zero.

In both models, diffusion of charged species is driven by the electrostatic potential, ideal solution thermodynamics, and phase equilibria across the phase boundary. The interfacial double layer is observed to develop naturally and agrees well with the classical Gouy-Chapman theory. The results of the sharp and diffuse interface models are compared in terms of physical accuracy and computational expense.

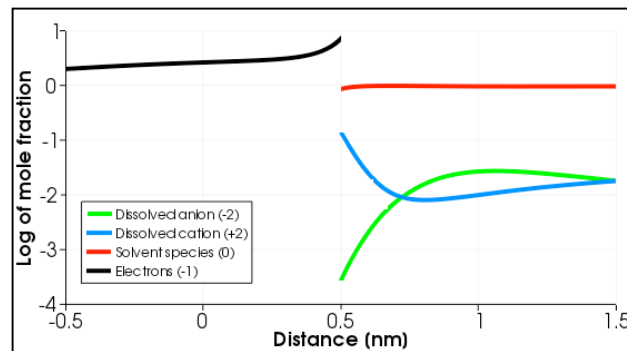


Figure: Sharp interface model showing mole fraction of mobile species after distribution due to Fickian and electro-diffusion. Electrode (right) contains only electrons, which crowd on the surface. The electrolyte (left) contains dissolved cations and anions, and a neutral solvent.

## REFERENCES

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